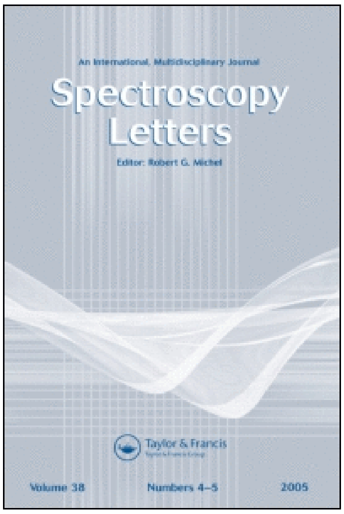

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3,3-Dimethyl-2-butanone: Infrared and Raman Spectra, Normal Coordinate Calculations, and Calculated Structure

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3,3-DIMETHYL-2-BUTANONE: INFRARED AND RAMAN SPECTRA, NORMAL COORDINATE CALCULATIONS, AND CALCULATED STRUCTURE

Keywords: 3,3-Dimethyl-2-butanone, Infrared spectra, Raman spectra, Normal coordinate analysis, Molecular structure calculations

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ABSTRACT

Infrared and Raman spectra were obtained for 3,3-dimethyl-2-butanone, and the spectra were interpreted with the aid of normal coordinate calculations. The spectra can be explained by the presence of only one conformation. The vibrational assignment and force constants that were obtained are given in this paper, along with some results of MM+, AM1, and PM3 semi-empirical molecular orbital calculations.

INTRODUCTION

Vibrational spectra have been published for several ketones, including acetone,[1] 2-butanone,[2,3] 2-pentanone,[3,4] 3-pentanone,[3,5] and 3-methyl-2-butanone.[6] Vibrational assignments or partial assignments were made for each of those ketones with the aid of normal coordinate calculations.[1,3,4-6] All those compounds, except for acetone, exhibit rotational isomerism. IR and Raman spectra have now been obtained, and normal coordinate calculations have been made, for 3,3-dimethyl-2-butanone (methyl-*t*-butyl ketone) in order to make a fundamental vibrational assignment for this compound. In addition, molecular mechanics and semi-empirical molecular orbital calculations have been made in order to compare the resulting calculated structures with the *ab initio*[7] structure.

EXPERIMENTAL

Infrared spectra were obtained at 2-cm^{-1} resolution with a Mattson 2020 FTIR spectrometer, which is equipped with a DTGS detector. Raman spectra were obtained at 4-cm^{-1} resolution with a SPEX double monochromator equipped with a Spectra-Physics Model 2020 argon-ion laser. The 514.5-nm line was used at ca. 100 mW power at the sample, which was contained in one-milliliter cell. The compound was obtained from Wiley Organics, and it had a stated purity of 99%. It was used without further purification.

CALCULATIONS

Normal coordinate calculations were made with the MOLVIB (Version 6.0) program,[8] which can handle the calculations for molecules with up to 30 atoms and 100 force constants. This program was written by Dr. Thomas Sundius of the University of Helsinki and distributed by Indiana University. A fifty-two parameter modified valence force field, which included twenty-three diagonal and twenty-nine interaction force constants, was used for 3,3-dimethyl-2-butanone. The molecular parameters that were used are: C=O = 0.1216 nm; C-C = 0.154 nm; =C-C = 0.1488 nm; C-H = 0.109 nm; and all angles were assumed to be 120° or 109.47°. A molecule of 3,3-dimethyl-2-butanone was assumed to belong to the C_s point group, with one of the methyls of the *t*-butyl group being *cis* to the oxygen, which is a normal stable conformation for ketones. Shimanouchi et al.[3] showed from electron diffraction data that one of the stable forms of 2-butanone is *trans* with respect to the two methyls and not with respect to the oxygen and methyl. Preliminary calculations for the conformation of 3,3-dimethyl-2-butanone with a methyl *trans* to the oxygen indicates a much higher energy than for the C_s conformer. *Ab initio* calculations have been made for this compound, as discussed later in this paper.

RESULTS AND DISCUSSION

Liquid-state IR and Raman spectra were obtained for this compound, but they are not shown here in order to conserve space. They are available from the author. It can be seen that the most intense Raman band is the 673-cm^{-1} band, which can be easily assigned to a C-C stretch of the *t*-butyl group. This band has only weak to medium-weak intensity in the IR spectrum. Also immediately noticable is the Raman band at 77 cm^{-1}, which can only be assigned to a torsional mode. It seems to be too low for a methyl torsion, so it must be due to the torsion about the C2-C3 bond.

Durig et al.[9] obtained IR spectra in the 400-30 cm^{-1} region for solid and gaseous 3,3-dimethyl-2-butanone, and they obtained the solid-state Raman spectrum in the 400-20 cm^{-1} region. They assigned methyl torsional modes to bands observed at 150, 218, 274, and 280 cm^{-1} (IR, solid). In addition, they assigned the CC_3 torsion to a strong band observed at 35 cm^{-1} in the gas-phase IR spectrum, at 100 cm^{-1} (strong) in the solid-phase IR spectrum, and at 106 cm^{-1} (weak) in the solid-phase Raman spectrum. The liquid-state Raman band that was observed at 77 cm^{-1} in the present work lies between the gas-phase and solid-phase values. Liquid-vapor frequency shifts have been observed in far-IR spectra in the past,[10] but not of the magnitude observed for the CC_3 torsion. For all eleven cases listed in ref. 10, the gas-state frequency is lower than for the liquid.

A molecule of 3,3-dimethyl-2-butanone should exist in only one stable conformation, so the vibrational assignment will be more straight-forward than for, e.g., 3-methyl-2-butanone, which exists in at least two stable conformations.[6,8] When more than one conformer exists, the observed bands must be assigned to each conformer, and complete assignments to all conformers can never be made with certainty, because there is always considerable frequency overlap between conformers.

Normal coordinate calculations have been made for the structurally similar molecule 2,3,3-trimethyl-1-butene.[12] Both molecules can be written $CH_3C(=X)C(CH_3)_3$, with X meaning either CH_2 or O. Initial force constants for 3,3-dimethyl-2-butanone were taken from this alkene for the t-butyl group and from 3-methyl-2-butanone[8] or acetone[1] for the $CH_3C=O$ group. The zero-order run with the transferred force constant values resulted in an average difference between observed and calculated wavenumbers of 8.6 cm^{-1}. However, four of the calculated values were in error by 20-30 cm^{-1}, and one was off by 39 cm^{-1}. Several computer runs were then made, with several force constants adjusted manually, until better agreement was obtained for those values that were in error by the largest amount. Then, several runs were made with different sets of force constants being adjusted. In the final run, thirty force constants were adjusted by the least-squares fit part of MOLVIB to fit forty-nine assigned wavenumbers, with the average error being 1.65 cm^{-1}. The observed and calculated wavenumbers and potential energy distributions in terms of symmetry coordinates are given in Table 1.

Only the two values calculated at 1017 and 1025 cm^{-1} (see Table 1) were not assigned to observed values. These two modes are nearly pure methyl rocks, and it is possible that they could overlap the 1038-cm^{-1} band, for which there are two calculated values. One of these was not used initially in the least-squares refinement, and it was calculated at 1032 cm^{-1}. It was therefore assigned to the 1038 cm^{-1} band and appropriate force constants were refined to fit the observed value. The force constants, their definitions, and their final values are given in Table 2.

Table 1 Observed and calculated wavenumbers and approximate potential energy distributions for 3,3-dimethyl-2-butanone

Obs. cm^{-1}	Calc. cm^{-1}	PED(%)[a]
2972	2974	CH_3 asym. str.(997
2972	2974	CH_3 asym. str.(99)
2972	2973	CH_3 asym. str.(99)
2972	2973	CH_3 asym. str.(100)
2972	2971	CH_3 asym. str.(100)
2972	2971	CH_3 asym. str.(97)
2972	2970	CH_3 asym. str.(96)
2972	2970	CH_3 asym. str.(100)
2929	2929	CH_3 sym. str.(100)
2911	2911	CH_3 sym. str. 100)
2878	2878	CH_3 sym. str.(100)
2878	2878	CH_3 sym. str.(100)
1710	1710	C=O str.(67), CCC def.(13)
1477	1477	CH_3 asym. def.(84),CH_3 rock(13)
1476	1476	CH_3 asym. def.(78),CH_3 rock(13)
1461	1461	CH_3 asym.def.(82),CH_3 rock(11)
1452	1455	CH_3 asym. def.(89)
1452	1453	CH_3 asym. def.(87)
1452	1451	CH_3 asym. def.(91)
1429	1430	CH_3 asym. def.(79)

(continued)

Table 1 (continued)

Obs. cm^{-1}	Calc. cm^{-1}	PED(%)[a]
1429	1426	CH_3 asym.def.(91)
1395	1395	CH_3 sym. def.(81)
1365	1370	CH_3 sym. def.(74)
1365	1365	CH_3 sym. def.(84)
1356	1352	CH_3 sym. def.(85)
1278	1277	C-C str.(36),CH_3 sym. def.(18), CH_3 rock(16)
1223	1220	C-C str.(32),CH_3 sym. def.(25), CH_3 rock(21)
1204	1208	C-C str.(44),CH_3 rock(24), CH_3 sym. def.(20)
1136	1133	CH_3 rock(41),C-C str.(34)
1047	1051	CH_3 rock(85)
1038	1039	CH_3 rock(86)
1038	1038	CH_3 rock(69),C=O str.(11)
--	1025	CH_3 rock(87)
--	1017	CH_3 rock(82)
955	947	C-C str.(49),CH_3 rock(43)
939	945	C-C str.(44),CH_3 rock(41)
833	839	C-C str.(77)
673	674	C-C str.(76)
554	554	CC_3 rock(50),C=O o-p bend(37)

Table 1 (continued)

Obs. cm^{-1}	Calc. cm^{-1}	PED(%)[a]
531	530	CCC def.(42),CH_3 rock(21), C-C str.(11)
459	459	C=O i-p def.(46),CCC def.(21), C-C str.(18)
371	372	CCC def.(86)
355	353	CCC def.(79)
306[b]	307	CCC def.(56),C=O i-p def.(18)
280[b]	285	CH_3 torsion(55),CCC def.(25), CC_3 rock(17)
274[b]	274	CH_3 torsion(96)
260[b]	255	CH_3 torsion(39),CC_3 rock(29), CCC def.(23)
236	235	CH_3 torsion(50),C=O o-p def.(24) CC_3 rock(20)
218[b]	212	CH_3 torsion(49),C=O o-p(29), CC_3 rock(18)
150[b]	150	CH_3 torsion[c](95)
77	77	$-C(CH_3)_3$ torsion(99)

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[a] Contributions less than 10% are excluded. Abbreviations used: asym. = antisymmetric; sym. = symmetric; str. = stretch; def. = deformation; o-p = out-of-plane; i-p = in-plane

[b] from ref. 9

[c] methyl torsion of the $=C-CH_3$ group

Table 2
Force constants for 3,3-dimethyl-2-butanone

Force Constant	Group	Atom(s) common	Value[a]
Stretch			
C-H	$=C-CH_3$	-	4.775
C-H	$C-CH_3$[b]	-	4.753
C-H	$C-CH_3$[c]	-	4.719
C-C	$=CC_2$	-	4.020
C-C	CC_3	-	4.418
C=O	C=O	-	9.748
Stretch-Stretch			
CH,CH	$=C-CH_3$	C	0.083
CH,CH	CH_3[b]	C	0.065
CH,CH	CH_3[c]	C	0.026
CC,CC	CC_3	C	0.239
CC,CC	$=CC_2$	C	0.350
=CC,CC	$=C-CC_3$	C	0.350
C=O,CC	$O=CC_2$[d]	=C	0.300
C=O,CC	$O=CC_2$[e]	=C	0.326
Bend			
H-C-H	$=C-CH_3$	-	0.510
H-C-H	CH_3[b]	-	0.540
H-C-H	CH_3[c]	-	0.528
C-C-H	$-C-CH_3$[b]	-	0.704
C-C-H	$-C-CH_3$[c]	-	0.647
C-C-H	$=C-CH_3$[f]	-	0.655
C-C-H	$=C-CH_3$[g]	-	0.694
O=C-C	O=CC	-	0.834
C-C-C	$C\overset{\|}{C}C$	-	1.649
=C-C-C	$=CCC_3$[b]	-	1.330

Table 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
=C-C-C	$=CCC_3$[c]	-	1.091
C-C-C	CC_3	-	1.029
C=O o-p	$C_2C=O$	-	0.214
<u>Stretch-Bend</u>			
=CC,CCH	$=C-CH_3$	C-C	0.270
CC,CCH	$C(CH_3)_3$	C-C	0.320
CC,CCC	CC_3	C-C	0.400
CC,CCC	$C-C-CC_3$	C-C	0.351
<u>Bend-Bend</u>			
CCH,CCH	$C-CH_3$[b]	C-C	-0.056
CCH,CCH	$C-CH_3$[c]	C-C	-0.050
CCH,CCH	$=C-CH_3$	C-C	-0.006
CCH,CCH	$=C-CH_3$[f]	C-C	-0.021
CCH,CCH	$C(CH_3)_3$	C-C	-0.044
CCO,CCO	$O=CC_2$	C-C	-0.020
CCC,CCC	CCC_3	C-C	-0.040
HCC, CCC trans	$CH_3-\overset{\parallel}{C}-C$	C-C	0.072
HCC, CCC gauche	$CH_3-\overset{\parallel}{C}-C$	C-C	-0.058
CCC, CCH trans	$=C-C-CH_3$[b]	C-C	-0.048
CCC, CCH gauche	$=C-C-CH_3$[b]	C-C	-0.119
CCC, CCH trans	$=C-C-CH_3$[c]	C-C	0.072
CCC, CCH gauche	$=C-C-CH_3$[c]	C-C	-0.058

(continued)

Table 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
OCC, CCC cis	O=C-C-C	C-C	0.250
CCC, CCC trans	$C-C-CC_3$	C-C	-0.011
CCC, CCC gauche	$C-C-CC_3$	C-C	-0.055
Torsion			
$-CH_3$	$=C-CH_3$	-	0.042
$-CH_3$	$C(CH_3)_3$	-	0.092[b]
$-CH_3$	$C(CH_3)_3$	-	0.137[c]
$-C(CH_3)_3$	$C-C(CH_3)_3$	-	0.119

[a] Stretching constants are in units of mdyn/Å; stretch-bend constants are in units of mdyn/rad; bending constants are in units of mdyn Å/rad^2.

[b] for methyl group cis to oxygen. [c] for two methyl groups gauche to carbon number 1. [d] C2-C3. [e] C1-C2 [f] for hydrogen cis to oxygen. [g] for the 2 hydrogens gauche to carbon number 3.

Schafer et al.[7] made *ab initio* calculations for 3,3-dimethyl-2-butanone at the 4-21G level. The C-C-C=O torsional angle (C4-C3-C2=O) was constrained at 0°, and some of the resulting optimized parameters, involving only C and O, are given in Table 3, along with MM+, AM1, and PM3 results from the current work. None of the torsional angles were constrained in the MM+, AM1, or PM3

Table 3 Partial MM+ and M.O. results for 3,3-dimethyl-2-butanone

Property	MM+	AM1	PM3	4-21G[a]
Bond lengths (Å)				
C2=O	1.211	1.235	1.215	1.2153
C1-C2	1.520	1.496	1.508	1.5231
C2-C3	1.534	1.523	1.539	1.5365
C3-C4[b]	1.544	1.523	1.527	1.5391
C3-C5	1.540	1.522	1.528	1.5480
C3-C6	1.540	1.522	1.528	1.5480
Angles (°)				
C1-C2=O	119.0	121.3	121.0	120.21
C1-C2-C3	119.6	117.1	116.6	118.57
C3-C2=O	121.4	121.6	122.4	121.22
C2-C3-C4	109.6	109.6	111.5	108.61
C2-C3-C5	109.8	109.4	109.0	109.69
C2-C3-C6	109.8	109.4	108.4	109.69
C4-C3-C5	108.7	109.1	108.9	109.58
C4-C3-C6	108.7	109.1	109.0	109.58
C5-C3-C6	110.2	110.2	109.9	109.66
Dihedral angles (°)				
C1-C2-C3-C4	180.0	180.0	-175.9	180.0
C1-C2-C3-C5	-60.6	-60.4	-55.6	-60.3
C1-C2-C3-C6	60.6	60.4	64.2	60.3
O=C2-C3-C4	0.0	0.0	4.5	0.0[c]
O=C2-C3-C5	119.4	119.6	124.8	119.7
O =C2-C3-C6	-119.4	-119.6	-115.5	-119.7
Heat of Formation (Kcal/mole)		-61.5	-67.1	

[a] Ref. 7 [b] C4 is cis to the oxygen
[c] Constrained

calculations, and the C4-C3-C2=O) angle was calculated to be 0° by MM+ and AM1.

Comparison of the *ab initio* results with MM+, AM1, and PM3 shows bond lengths calculated with MM+ to be better than with AM1 or PM3. The PM3 bond lengths are a little better than AM1. MM+ and AM1 bond angles and dihedral angles are comparable to each other and are better than the PM3 angles. It should be noted that the MM+, AM1, and *ab initio* results maintain the C_s symmetry of the molecule, but PM3 does not. It can also be seen that the MM+ results are very to the *ab initio* results.

Schafer et al.[7] also made *ab initio* calculations for a conformation of 3,3-dimethyl-2-butanone that has the C4-C3-C2=O torsional angle constrained to 180° (C=O bond bisects C5-C3-C6 angle). However, there is no reason to believe that this conformation is stable, and it was not considered here. All observed IR and Raman bands can be explained by the presence of only the C_s conformer.

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